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PRODUCTION OF ALUMINOSILICATE GLASS CONTAINING RARE EARTH METAL

[*Kidorui ganyuh aruminokeisanen garasuno seizoh houhoh*]

Inventor(s):	Akio Makishima 500-10 Shimo Hirokawa Sakura-mura, Shingi-gun Ibaragi-ken
	Hajime Kubo 1-28-3 Izumi Suginami-ku, Tokyo

Kohjiroh Shimodaira
441-3 Yukitani-cho
Kodori, Tatsugasaki-shi

Applicant(s): Chief of Inorganic Materials Research Inst. Science and Technology Agency

[There are no amendments to this patent.]

Specification

Title of the invention

Production of aluminosilicate glass containing rare earth metal

Claims of the invention

1) A method for production of aluminosilicate glass containing rare earth metal characterized by the fact that 30 to 53 wt% of secondary shirasu, 9 to 30 wt% of Al_2O_3 and 23 to 54 wt% of Y_2O_3 concentrate are used as raw materials, and the mixture thereof is made molten under heat and vitrified.

2) A method for production of aluminosilicate glass characterized by the fact that 13 wt% or less of TiO_2 or 9 wt% or less of ZrO_2 is used in addition to 30 to 53 wt% of secondary shirasu, 9 to 30 wt% of Al_2O_3, and 23 to 54 wt% of Y_2O_3 concentrate and made molten under heat and vitrified.

Detailed description of the invention

Field of industrial application

The present invention pertains to a method of manufacturing aluminosilicate glass containing a rare earth metal produced as melting is done at a temperature of 1550°C or below.

Prior art

Aluminosilicate glass consisting of silica and alumina has high heat-resistance, excellent mechanical strength, and high corrosion resistance and resistance to weathering. However, a very high temperature is required to produce the aforementioned glass. The temperature limit of electric furnaces where standard silicon carbide heating elements are used is approximately 1550°C; thus, production of the aforementioned glass has not been possible by the hot-melt method using standard electric furnaces.

In general, when an alkali oxide and alkali earth oxide are included, the hot-melt temperature is reduced and production of a glass using an electric furnace with standard silicon carbide heating elements is possible at a temperature of approximately 1550°C. However, when an alkali oxide and an alkali earth oxide are included, a reduction occurs in properties such as heat-resistance, mechanical properties, chemical resistance, corrosion resistance and resistance to weathering.

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The present inventors discovered that a glass could be produced at a temperature of approximately 1550°C using a standard electric furnace when Y_2O_3 was included and that the glass produced had high mechanical strength [Journal of Industrial Society of America, Vol. 61, pp. 247-249 (1978)]. However, separated Y_2O_3 is expensive and a cost increase is inevitable.

In order to eliminate the aforementioned problem, a study was conducted by the present inventors on the use of yttrium concentrate, used as an intermediate in the production of Y_2O_3, and, as a result, the discovered that an ore of Y_2O_3, for example, a yttrium concentrate made of purified zenotime consists of several tens of percent of Y_2O_3, and rare earth oxides such as Dy_2O_3, Nd_2O_3, CeO_2, Ho_2O_3, Yb_2O_3, Sm_2O_3, La_2O_3, Gd_2O_3 and Er_2O_3, and that the aforementioned material was used instead of Y_2O_3 and an aluminosilicate glass was produced, (1) properties, in particular, alkali resistance of the aluminosilicate glass are not adversely influenced by impurities other than Y_2O_3, and (2) the melting point of the glass could be reduced

by approximately 50°C compared to the case where the aforementioned Y_2O_3 was used, and that the cost could be reduced by 1/5 (Japanese Patent Application No. Sho 57-180498).

Continuing research on cost reduction was done by the present inventors, and as a result, they discovered that the shirasu of volcanic ash widely scattered on the island of Kyushu [Japan] included a vitreous aluminosilicate material as the main component, and that the chemical composition of the secondary shirasu, which were in the secondary deposits of shirasu, was substantially constant, and further research was conducted. The chemical composition of the secondary shirasu is as shown below.

SiO_2	82.59 mol%	75.87 wt%
Al_2O_3	9.16 "	14.28 "
Fe_2O_3	0.92 "	2.24 "
CaO	1.54 "	1.32 "
MgO	0.49 "	0.30 "
Na_2O	3.35 "	3.18 "
K_2O	1.95 "	2.80 "

As shown above, the sum of SiO_2 and Al_2O_3 is approximately 92 mol%, and the majority of that is aluminosilicate. When glass was produced using the Y_2O_3 concentrate, secondary shirasu, and Al_2O_3 as raw materials, a glass containing the aforementioned components and approximately 5 mole % or less of Fe_2O_3, CaO, MgO, Na_2O and K_2O is included in the aforementioned secondary shirasu and the amounts are listed in the aforementioned table for the total that was produced. Furthermore, when the aforementioned are used as raw materials, vitrification time could be reduced to approximately 1/3 in comparison to the case where only SiO_2 and Al_2O_3 were used as raw materials.

The present invention is a method for production of aluminosilicate glass containing rare earth metal characterized by the fact that 30 to 53 wt% of secondary shirasu, 9 to 30 wt% of Al_2O_3 and 23 to 54 wt% of Y_2O_3 concentrate are used as raw materials, and the mixture of the same is molten under heat and vitrified.

Y_2O_3 concentrate used in the present invention is an ore of Y_2O_3, for example, an intermediate product of zenotime produced by the sulfuric acid decomposition method or alkali decomposition method. In the case of the alkali decomposition method, the zenotime is added slowly to 400°C molten caustic soda. The reaction is exothermic and cooling is done after the reaction and the reaction product is extracted in water and sodium phosphate and excessive alkali is removed. The rare earth hydroxide produced is dissolved in a small amount of hydrochloric acid, then, oxalic acid is added to the aforementioned solution to form a rare oxalate, and when baking is done at a temperature of 900°C, the yttrium concentrate is produced. An analysis example is shown below.

Analysis example of yttrium concentrate (%)

Rare earth base		Rare earth base	
Y_2O_3	62.9%	Sm_2O_3	1.4
CeO_2	3.14	Nd_2O_3	4.3
La_2O_3	2.23	Pr_2O_3	0.88
Eu_2O_3	0.02	ThO_2	<0.2
Gd_2O_3	2.7	Rare Earth	98.0%
Dy_2O_3	11.3	IgLoss	0.2
Er_2O_3	1.43	CaO	<0.2
Ho_2O_3	3.8	SO_3	<0.5
Yb_2O_3	5.0	P_2O_5	<0.1

In other words, component substances are included in the ore without separation.

When the amount of the secondary shirasu included in the glass raw material of the present invention is 30 wt% or below, the hot-melt temperature is increased and vitrification is not possible at 1550°C. On the other hand, when the aforementioned amount exceeds 53 wt%, properties of an aluminosilicate glass containing rare earth cannot be achieved.

When the amount of Al_2O_3 is below 9 wt%, vitrification is not possible. On the other hand, when the amount exceeds 30 wt%, the hot-melt temperature is increased and vitrification is not possible at 1550°C.

When the amount of Y_2O_3 concentrate is 23 wt% or below, properties of a glass containing a rare earth oxide cannot be achieved and vitrification is not possible at 1550°C. On the other hand, when the amount exceeds 54 wt%, crystallization occurs and a glass cannot be produced.

Therefore, 30 to 53 wt% of secondary shirasu, 9 to 30 wt% of Al_2O_3 and 23 to 54 wt% of Y_2O_3 concentrate are required.

In addition to the aforementioned raw materials, 13 wt% or less of TiO_2 or 9 wt% or less of ZrO_2 may be used, as needed. When TiO_2 is added, increase in chemical resistance, corrosion resistance, and resistance to weathering can be achieved, but when the amount added exceeds 13 wt%, crystallization occurs and a glass cannot be produced. When ZrO_2 is added, an increase in chemical resistance, corrosion resistance, resistance to weathering, mechanical properties, and heat-resistance can be achieved, but when the amount added exceeds 9 wt%, crystallization occurs and a glass cannot be produced.

The above-mentioned raw materials are molten at a temperature of 1550°C or below and vitrified to produce an aluminosilicate glass containing rare earth.

Working Example 1

A mixture consisting of 51.93 wt% of secondary shirasu, 12.60 wt% of Al_2O_3, and 35.47 wt% of Y_2O_3 concentrate was placed in a platinum crucible, made molten in an electric furnace for 2 hours at a temperature of 1500°C, and then, cast onto an aluminum sheet to cool naturally. A light brown transparent glass with an absence of air bubbles was produced.

The thermal expansion factor of the above-mentioned glass produced was 53.1×10^{-7} 1/°C, and the degree of thermal expansion is significantly lower than that of standard window glasses. Thus, impact resistance is higher than that of standard soda-lime glass (thermal expansion factor of approximately 90×10^{-7} 1/°C) when used as a window glass. The aforementioned platinum crucible was removed from the furnace while the aforementioned glass is in a molten state and manually formed into a glass fiber, formation of a glass fiber with a thickness in the range of several microns to several mm and a length of 1 m or longer was easily achieved. A hard glass with a density of 3.258 g/cm^3 and Vickers hardness of 860 Kg/mm was produced.

Based on the raw material ratios calculated, the chemical composition of the aforementioned glass was 39.40 wt% (hereinafter referred to as %) of SiO_2, 20.02% of Al_2O_3, 1.16% of Fe_2O_3, 0.69% of CaO, 0.16% of MgO, 1.65% of NaO, 1.45% of K_2O, and 35.47% of yttrium concentrate.

Working Example 2

A mixture consisting of 36.08 wt% of secondary shirasu, 26.03 wt% of Al_2O_3, and 37.89 wt% of yttrium concentrate was placed in a platinum crucible, made molten in an electric furnace for 1.5 hours at a temperature of 1450°C; then, the temperature of the electric furnace was increased to 1500°C and hot-melting was done for 20 minutes, and then, the material was cast onto an aluminum sheet to cool naturally. A light brown transparent glass was produced. The thermal expansion factor of the glass produced was 53.0×10^{-7} 1/°C, and the density was 3.456 g/cm^3.

Working Example 3

A mixture consisting of 40.28 wt% of secondary shirasu, 17.53 wt% of Al_2O_3, and 42.19 wt% of yttrium concentrate was placed in a platinum crucible, molten in an electric furnace for 1.5 hours at a temperature of 1500°C, and then, cast onto an aluminum sheet to cool naturally. A light brown transparent glass with an absence of air bubbles was produced. The thermal expansion factor of the glass produced was 59.2×10^{-7} 1/°C, and the density was 3.521 g/cm^3. Furthermore, as in the case of Working Example 1, formation of fiber was achieved easily from the glass produced.

Working Example 4

A mixture consisting of 30.19 wt% of secondary shirasu, 18.26 wt% of Al_2O_3, 40.00 wt% of yttrium concentrate, and 11.55 wt% of TiO_2 was placed in a platinum crucible, made molten in an electric furnace for 1.5 hours at a temperature of 1550°C, and then, cast onto an aluminum sheet to cool naturally.

A reddish brown transparent glass with an absence of air bubbles was produced. The thermal expansion factor of the glass produced was 56×10^{-7} 1/°C, and the density was 3.612 g/cm^3.

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Working Example 5

A mixture consisting of 35.12 wt% of secondary shirasu, 17.06 wt% of Al_2O_3, 39.11 wt% of yttrium concentrate, and 8.71 wt% of ZrO_2 was placed in a platinum crucible and made molten in an electric furnace for 1.5 hours at a temperature of 1550°C. Furthermore, the aforementioned molten material was cast onto an aluminum sheet to cool naturally. A light brown transparent glass with an absence of air bubbles was produced. The thermal expansion factor of the glass produced was 53.0×10^{-7} 1/°C, and the density was 3.621 g/cm^3.

Effect of the invention

According to the method of the present invention, secondary shirasu and yttrium concentrate are used; as a result, an aluminosilicate containing Y_2O_3 can be produced at a low

cost, and furthermore, melting can be done in a standard electric furnace since the hot-melt temperature is low, heating time is reduced, and the glass produced retains the superior properties of aluminosilicate glass. Furthermore, the glass produced has high modulus and alkali resistance is high; thus, the glass can be used with cement as a composite. And furthermore, Fe_2O_3 and CeO_2 are included, thus, good ultraviolet absorption can be achieved, and therefore, the glass can be used effectively as window glass for sunrooms, sunroofs of automobiles, ultraviolet-absorbing containers for chemical and scientific use, and as a window material.

Applicant: Y. Gotoh, Chief of Inorganic Material Research Inst. Science and Technology Agency

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